Chapter 3
Biofuels

3.1 Introduction

The term biofuel refers to liquid, gas and solid fuels predominantly produced from biomass. Biofuels are important as they affect a wide array of topics, including energy security, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Biofuels include bioethanol, biomethanol, vegetable oils, biodiesel, biogas, biosynthetic gas (biosyngas), bio-oil, biochar, Fischer–Tropsch liquids, and biohydrogen.

There are two global biomass-based liquid transportation fuels that might replace gasoline and diesel fuel. These are bioethanol and biodiesel. World production of biofuel was about 68 billion liters in 2007. The primary feedstocks of bioethanol are sugarcane and corn. Bioethanol is a gasoline additive/substitute. Bioethanol is by far the most widely used biofuel for transportation worldwide. About 60% of global bioethanol production comes from sugarcane and 40% from other crops. Biodiesel refers to a diesel-equivalent mono-alkyl ester-based oxygenated fuel. Biodiesel production using inedible vegetable oil, waste oil and grease has become more attractive recently. The economic performance of a biodiesel plant can be determined once certain factors are identified, such as plant capacity, process technology, raw material cost and chemical costs. The central policy of biofuel concerns job creation, greater efficiency in the general business environment, and protection of the environment.

Biofuels offer a number of technical and environmental benefits over conventional fossil fuels, which make them attractive as alternatives for the transport sector. The benefits include greenhouse gas reductions including reduced carbon dioxide emissions, which will contribute to domestic and international targets, the diversification of the fuel sector, biodegradability, sustainability, and an additional market for agricultural products. Biofuels help to protect and create jobs. Table 3.1 shows the major benefits of biofuels.

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Table 3.1 Major benefits of biofuels

Economic impacts	Sustainability
	Fuel diversity
	Increased number of rural manufacturing jobs
	Increased income taxes
	Increased investments in plant and equipment
	Agricultural development
	International
	Reducing the dependency on imported petroleum
Environmental impacts	Greenhouse gas reductions
	Reducing of air pollution
	Biodegradability
	Higher combustion efficiency
	Improved land and water use
	Carbon sequestration
Energy security	Domestic targets
	Supply reliability
	Reducing use of fossil fuels
	Ready availability
	Domestic distribution
	Renewability

According to a study by the European Commission, European production of biofuels equivalent to 1% of EU automotive fuel consumption would help to protect and/or create between 45 000 and 75 000 jobs. Biofuels can be used as an alternative fuel for transport, as can other alternatives such as liquid natural gas (LNG), compressed natural gas (CNG) and liquefied petroleum gas (LPG). In the longer term, significant use of biofuels could offer large carbon savings. Policy drivers for renewable liquid biofuels have attracted particularly high levels of assistance in some countries given their promise of benefits in several areas of interest to governments, including agricultural production, greenhouse gas emissions, energy security, trade balances, rural development and economic opportunities for developing countries (Demirbas, 2008a).

First generation biofuels refer to biofuels made from sugar, starch, vegetable oils, or animal fats using conventional technology. The basic feedstocks for the production of first generation biofuels are often seeds or grains such as wheat, which yields starch that is fermented into bioethanol, or sunflower seeds, which are pressed to yield vegetable oil that can be used in biodiesel. Table 3.2 shows the classification of renewable biofuels based on their production technologies.

Table 3.2 Classification of renewable biofuels based on their production technologies

Generation	Feedstock	Example
First generation biofuels	Sugar, starch, vegetable oils, or animal fats	Bioalcohols, vegetable oil, Biodiesel, biosyngas, biogas
Second generation biofuels	Non-food crops, wheat straw, corn, wood, solid waste, energy crop	Bioalcohols, bio-oil, bio-DMF, Biohydrogen, bio-Fischer–Tropsch diesel, wood diesel
Third generation biofuels	Algae	Vegetable oil, biodiesel
Fourth generation biofuels	Vegetable oil, biodiesel	Biogasoline

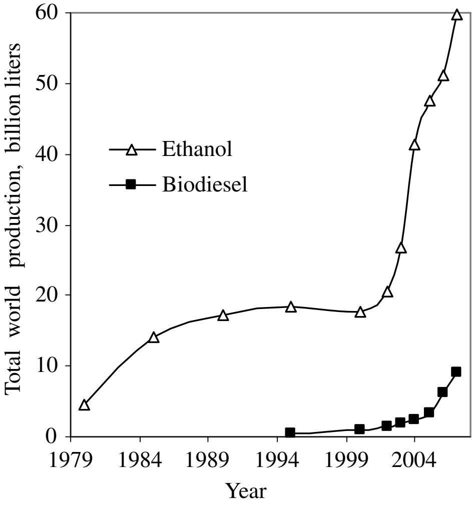

Fig. 3.1 World production of ethanol and biodiesel, 1980–2007

Second and third generation biofuels are also called advanced biofuels. Second generation biofuels made from non-food crops, wheat straw, corn, wood, energy crop using advanced technology. Algae fuel, also called oilgae or third generation biofuel, is a biofuel from algae. Algae are low-input/high-yield (30 times more energy per acre than land) feedstocks to produce biofuels using more advanced technology. On the other hand, an appearing fourth generation is based in the conversion of vegoil and biodiesel into biogasoline using the most advanced technology.

Figure 3.1 shows the world productions of ethanol and biodiesel between 1980 and 2007 (Demirbas, 2008a). Between 1991 and 2001, world ethanol production rose from around 16 billion liters a year to 18.5 billion liters. From 2001 to 2007, production is expected to have tripled, to almost 60 billion liters a year. Brazil was the world's leading ethanol producer until 2005 when U.S. production roughly

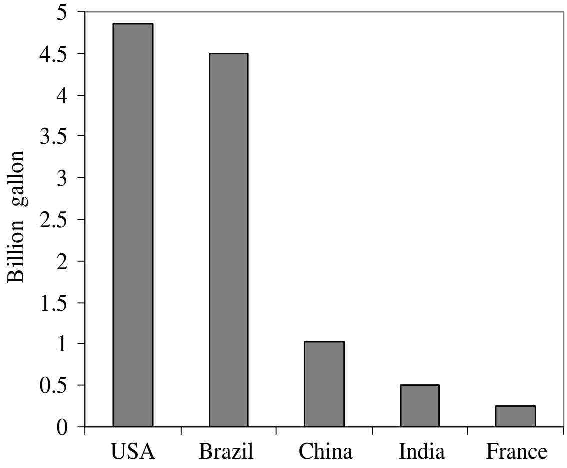

Fig. 3.2 The top five bioethanol producers (billion gallons) in 2006

equaled Brazil's. The United States became the world's leading ethanol producer in 2006. China holds a distant but important third place in world rankings, followed by India, France, Germany and Spain. Figure 3.2 shows the top five bioethanol producers in 2006 (RFA, 2007).

3.2 Bioethanol

Nowadays ethanol is the most popular fuel. Bioethanol is ethyl alcohol, grain alcohol, or chemically C_2H_5OH or EtOH. The use of ethanol as a motor fuel has as long a history as the car itself. Ethanol can be produced from cellulose feedstocks such as corn stalks, rice straw, sugar cane bagasse, pulpwood, switchgrass, and municipal solid waste is called bioethanol. Bioethanol is a renewable green fuel. Bioethanol is produced by fermentation of sugars, which can be obtained from natural sugars (e.g., sugar cane, sugar beet), starches (e.g., corn, wheat), or cellulosic biomass (e.g., corn stover, straw, grass, wood). The most common feedstock is sugar cane or sugar beet, and the second common feedstock is corn starch.

Currently, cellulosic biomass use is very limited due to the expensive pretreatment required for breaking the crystalline structure of cellulose. Bioethanol is already an established commodity due to its ongoing non-fuel uses in beverages, and in the manufacture of pharmaceuticals and cosmetics. In fact, ethanol is the oldest synthetic organic chemical used by mankind. Table 3.3 shows ethanol production in different continents (Demirbas, 2008b).

Bioethanol can be used as a 10% blend with gasoline without need for any engine modification. However, with some engine modification, bioethanol can be used at higher levels, for example, E85 (85% bioethanol).

Table 3.3 Ethanol production in different continents (billion liters/year) in 2006

America	Asia	Europe	Africa	Oceania
22.3	5.7	4.6	0.5	0.2

Bioethanol currently accounts for more than 94% of global biofuel production, with the majority coming from sugarcane. About 60% of global bioethanol production comes from sugarcane and 40% from other crops. Brazil and the United States are the world leaders, which together accounted for about 70% of the world bioethanol production exploiting sugarcane and corn respectively. Ethanol has been used in Germany and France as early as 1894 by the then incipient industry of internal combustion engines. Brazil has utilized ethanol as a fuel since 1925. Currently, ethanol is produced from sugar beets and from molasses. A typical yield is 72.5 l of ethanol per ton of sugar cane. Modern crops yield 60 tons of sugar cane *per* hectare of land. Production of ethanol from biomass is one way to reduce both the consumption of crude oil and environmental pollution. The use of gasohol (an ethanol and gasoline mixture) as an alternative motor fuel has been steadily increasing in the world for a number of reasons. Domestic production and use of ethanol for fuel can decrease dependence on foreign oil, reduce trade deficits, create jobs in rural areas, reduce air pollution, and reduce global climate change carbon dioxide build-up (Bala, 2005).

Bioethanol can be produced from a large variety of carbohydrates with a general formula of $(CH_2O)_n$. Fermentation of sucrose is performed using commercial yeast such as *Saccharomyces cerevisiae*. The chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars (Baltz et al., 1982; Sokhansanj et al., 2002; Kim and Dale, 2005). First, invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose. Second, *zymase*, another enzyme also present in the yeast, converts the glucose and the fructose into ethanol. A major processing step in an ethanol plant is enzymatic saccharification of cellulose to sugars through treatment by enzymes; this step requires lengthy processing and normally follows a short-term pre-treatment step (Kumar et al., 2005).

3.3 Other Bioalcohols

The alcohols that can be used for motor fuels are methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH), and butanol (C_4H_9OH). However only the first two of the alcohols are technically and economically suitable as fuels for internal combustion engines (ICEs). Main commercial bioalcohols from renewable feedstocks are bioethanol and biomethanol in the world's energy market.

Methanol is known as "wood alcohol." Generally, methanol is easier to find than ethanol. Sustainable methods of methanol production are currently not economically viable. Methanol is produced from synthetic gas or biogas and evaluated as a fuel for internal combustion engines. The production of methanol is a cost-intensive chemical process.

Methanol is another possible replacement for conventional motor fuels. In fact, it has been considered as a possible large-volume motor fuel substitute at various times during gasoline shortages. In fact, it was often used in the early twentieth century to power automobiles before introduction of inexpensive gasoline. Later, synthetically produced methanol was widely used as a motor fuel in Germany during World War II. Again, during the oil crisis of 1970s, methanol blending with motor fuel received attention due to its availability and low cost. Methanol is poisonous and burns with an invisible flame. Similar to ethanol, methanol has a high octane rating and hence is suitable for the Otto engine. Today, methanol is commonly used in biodiesel production for its reactivity with vegetable oils. Methanol can be used as one possible replacement for conventional motor fuels. Many tests have shown promising results using 85–100% by volume methanol as a transportation fuel in automobiles, trucks and buses.

Before 1920s, methanol was obtained from wood as a co-product of charcoal production, hence the name wood alcohol. Methanol is currently manufactured worldwide from syngas, which is derived from natural gas, refinery off-gas, coal or petroleum, as:

$$2H_2 + CO \rightarrow CH_3OH \tag{3.1}$$

The above reaction can be carried out in the presence of a variety of catalysts including Ni, Cu/Zn, Cu/SiO_2, Pd/SiO_2, and Pd/ZnO. In the case of coal, it is first pulverized and cleaned, then fed to a gasifier bed where it is reacted with oxygen and steam to produce the syngas. A 2:1 mole ratio of hydrogen to carbon monoxide is fed to a fixed-catalyst bed reactor for methanol production. Also, the technology for making methanol from natural gas is already in place and in wide use. Current natural gas feedstocks are so inexpensive that even with tax incentives renewable methanol has not been able to compete economically.

The composition of biosyngas from biomass is shown in Table 3.4. The hydrogen to CO ratio in biosyngas is less than that from coal or natural gas, hence additional hydrogen is needed for full conversion to methanol. The gases produced from biomass can be steam reformed to produce hydrogen and followed by water–gas shift reaction to further enhance the hydrogen content. Wet biomass can be easily

Table 3.4 Composition of biosyngas from biomass gasification

Constituents	Percentage by volume (dry and nitrogen-free)
Carbon monoxide (CO)	28–36
Hydrogen (H_2)	22–32
Carbon dioxide (CO_2)	21–30
Methane (CH_4)	8–11
Ethene (C_2H_4)	2–4

Table 3.5 Main production facilities of methanol and biomethanol

Methanol	Biomethanol
Catalytic synthesis from CO and H_2	Catalytic synthesis from CO and H_2
Natural gas	Distillation of liquid from wood pyrolysis
Petroleum gas	Gaseous products from biomass gasification
Distillation of liquid from coal pyrolysis	Synthetic gas from biomass and coal

gasified using supercritical water conditions. Main production pathways for methanol and biomethanol are compared in Table 3.5.

Methanol can be produced from biomass, essentially any primary energy source. Thus, the choice of fuel in the transportation sector is to some extent determined by the availability of biomass. As regards to the difference between hydrogen and methanol production costs, conversion of natural gas, biomass and coal into hydrogen is generally more energy efficient and less expensive than the conversion into methanol.

3.4 Biorefinery

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass. Biorefinery is the co-production of a spectrum of bio-based products and energy from biomass. The biorefinery concept is analogous to today's crude oil refinery. Biorefinery is a relatively new term referring to the conversion of biomass feedstock into a host of valuable chemicals and energy with minimal waste and emissions.

Biorefinery includes fractionation for separation of primary refinery products. The fractionation refers to the conversion of wood into its constituent components (cellulose, hemicelluloses and lignin). Processes include steam explosion, aqueous separation and hot water systems. Commercial products of biomass fractionation include levulinic acid, xylitol and alcohols. Figure 3.3 shows the fractionation of wood and chemicals from wood.

Main fractionation chemicals from wood ingredients are:

1. Dissociation of cell components → Lignin fragment + Oligosaccharides + Cellulose
2. Hydrolysis of cellulose (saccharification) → Glucose
3. Conversion of glucose (fermentation) → Ethanol + Lactic acid
4. Chemical degradation of cellulose → Levulinic acid + Xylitol
5. Chemical degradation of lignin → Phenolic products

Biorefinery is the process of extracting valuable chemicals and polymers from biomass. The main technologies to produce chemicals from biomass are: (a) biomass refining or pre-treatment, (b) thermochemical conversion (gasification, pyrolysis,

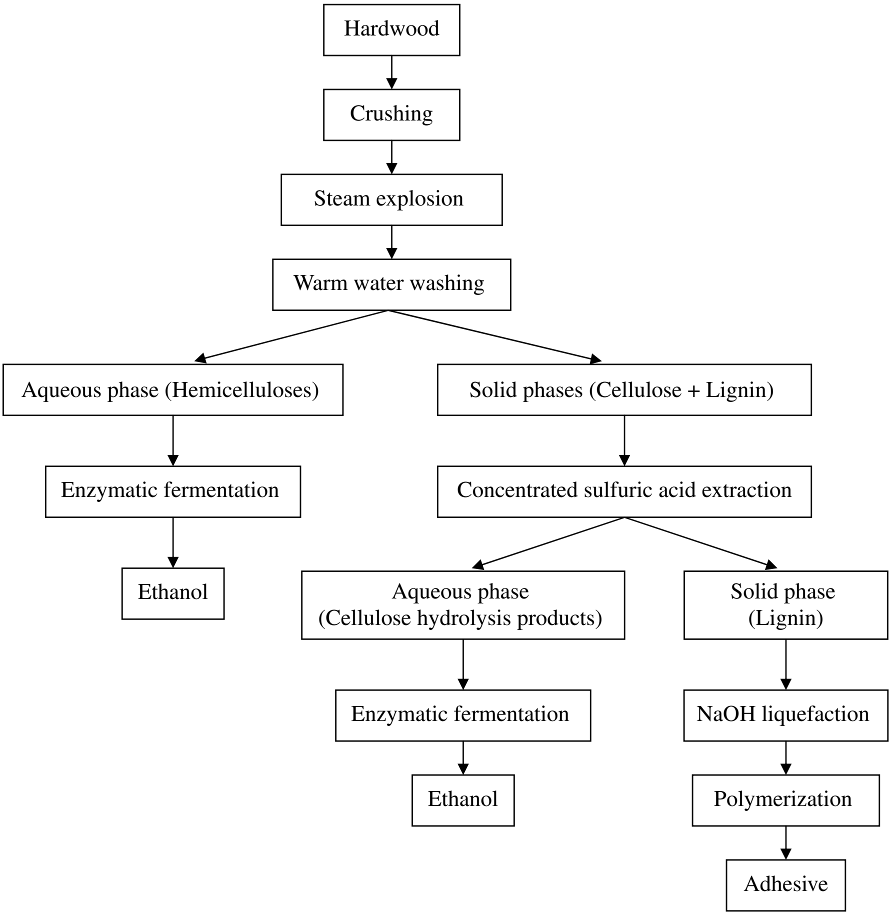

Fig. 3.3 Fractionation of wood and chemicals from wood

hydrothermal upgrading), (c) fermentation and bioconversion, and (d) product separation and upgrading.

There are four main biorefineries: biosyngas-based refinery, pyrolysis-based refinery, hydrothermal upgrading-based refinery, and fermentation-based refinery. Biosyngas is a multifunctional intermediate for the production of materials, chemicals, transportation fuels, power and/or heat from biomass. Figure 3.4 shows the gasification-based thermochemical biorefinery.

Pyrolysis oil (bio-oil) is produced in fast and flash pyrolysis processes and can be used for indirect co-firing for power production in conventional power plants and potentially as a high energy density intermediate for the final production of chemicals and/or transportation fuels. Gas chromatographic analysis of the liquid fraction of pyrolysis products from beech wood is given in Table 3.6 (Demirbas, 2007). Biocrude results from severe hydrothermal upgrading (HTU) of relatively wet biomass and potentially can be used for the production of materials, chemicals,

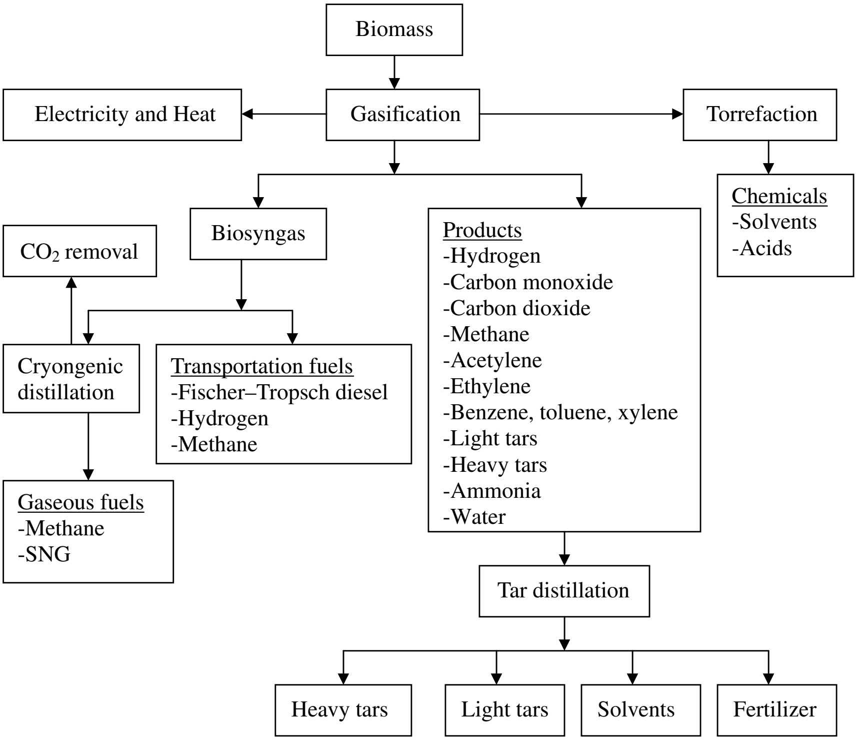

Fig. 3.4 Gasification-based thermochemical biorefinery

transportation fuels, power and/or heat. Mixed sugars resulting from fermentation (C_5 and C_6 sugars) are further refined substrates for chemical and bioconversion.

The bio-oil formed at 725 K contains high concentrations of compounds such as acetic acid, 1-hydroxy-2-butanone, 1-hydroxy-2-propanone, methanol, 2,6-dimethoxyphenol, 4-methyl-2,6-dimetoxyphenol and 2-Cyclopenten-1-one, etc. A significant characteristic of bio-oils was the high percentage of alkylated compounds especially methyl derivatives. The structural components of the biomass samples mainly have an effect on pyrolytic degradation products. A reaction mechanism is proposed which describes a possible reaction route for the formation of the characteristic compounds found in the oils. The supercritical water extraction and liquefaction partial reactions also occur during the pyrolysis. The phenol content increased to 52% and the yield of neutral oils increased from 18 to 33% with increasing temperature, while the methoxyl content decreased. The methoxyl content at 675 K amounted to 11.8%, at 875 K to only 5%. The coke formed could be briquetted without the addition of a binder. It has been reported that the first runs in the pyrolysis of the pyroligneous acid consists of about 50% methanol, 18% acetone, 7% esters, 6% aldehydes, 0.5% ethyl alcohol, 18.5% water, and small amounts of furfural (Demirbas, 2007).

Table 3.6 Gas chromatographic analysis of the liquid fraction of pyrolysis products from beech wood (wt.% dry basis)

Compound	Reaction temperature (K)					
	625	675	725	775	825	875
Acetic acid	16.8	16.5	15.9	12.6	8.42	5.30
Methyl acetate	0.47	0.35	0.21	0.16	0.14	0.11
1-Hydroxy-2-propanone	6.32	6.84	7.26	7.66	8.21	8.46
Methanol	4.16	4.63	5.08	5.34	5.63	5.82
1-Hydroxy-2-butanone	3.40	3.62	3.82	3.88	3.96	4.11
1-Hydroxy-2-propane acetate	1.06	0.97	0.88	0.83	0.78	0.75
Levoglucosan	2.59	2.10	1.62	1.30	1.09	0.38
1-Hydroxy-2-butanone acetate	0.97	0.78	0.62	0.54	0.48	0.45
Formic acid	1.18	1.04	0.84	0.72	0.60	0.48
Guaiacol	0.74	0.78	0.82	0.86	0.89	0.93
Crotonic acid	0.96	0.74	0.62	0.41	0.30	0.18
Butyrolactone	0.74	0.68	0.66	0.67	0.62	0.63
Propionic acid	0.96	0.81	0.60	0.49	0.41	0.34
Acetone	0.62	0.78	0.93	1.08	1.22	1.28
2,3-Butanedione	0.46	0.50	0.56	0.56	0.58	0.61
2,3-Pentanedione	0.34	0.42	0.50	0.53	0.59	0.64
Valeric acid	0.72	0.62	0.55	0.46	0.38	0.30
Isovaleric acid	0.68	0.59	0.51	0.42	0.35	0.26
Furfural	2.52	2.26	2.09	1.84	1.72	1.58
5-Methyl-furfural	0.65	0.51	0.42	0.44	0.40	0.36
Butyric acid	0.56	0.50	0.46	0.39	0.31	0.23
Isobutyric acid	0.49	0.44	0.38	0.30	0.25	0.18
Valerolactone	0.51	0.45	0.38	0.32	0.34	0.35
Propanone	0.41	0.35	0.28	0.25	0.26	0.21
2-Butanone	0.18	0.17	0.32	0.38	0.45	0.43
Crotonolactone	0.12	0.19	0.29	0.36	0.40	0.44
Acrylic acid	0.44	0.39	0.33	0.25	0.19	0.15
2-Cyclopenten-1-one	1.48	1.65	1.86	1.96	2.05	2.13
2-Methyl-2-cyclopenten-1-one	0.40	0.31	0.24	0.17	0.13	0.14
2-Methyl-cyclopentenone	0.20	0.18	0.17	0.22	0.25	0.29
Cyclopentenone	0.10	0.14	0.16	0.23	0.27	0.31
Methyl-2-furancarboxaldehyde	0.73	0.65	0.58	0.50	0.44	0.38
Phenol	0.24	0.30	0.36	0.43	0.54	0.66
2,6-Dimethoxyphenol	2.28	2.09	1.98	1.88	1.81	1.76

Table 3.6 (*continued*)

Compound	Reaction temperature (K)					
	625	675	725	775	825	875
Dimethyl phenol	0.08	0.13	0.18	0.42	0.64	0.90
Methyl phenol	0.32	0.38	0.44	0.50	0.66	0.87
4-Methyl-2,6-dimetoxyphenol	2.24	2.05	1.84	1.74	1.69	1.58

3.5 Biodiesel

Fossil fuel resources are decreasing daily. Biodiesel is attracting increasing attention worldwide as blending components or direct replacements for diesel fuel in vehicle engines. Biodiesel typically comprises lower alkyl fatty acid (chain length C_{14}–C_{22}), esters of short-chain alcohols, primarily, methanol or ethanol. Various methods have been reported for the production of biodiesel from vegetable oil, such as direct use and blending, microemulsification, pyrolysis, and transesterification. Among these, transesterification is an attractive and widely accepted technique. The purpose of the transesterification process is to lower the viscosity of the oil. The most important variables affecting methyl ester yield during the transesterification reaction are the molar ratio of alcohol to vegetable oil and the reaction temperature. Methanol is the commonly used alcohol in this process, due in part to its low cost. Methyl esters of vegetable oils have several outstanding advantages over other new renewable and clean engine fuel alternatives.

The interest in fatty acid methyl esters based on biodiesel has grown considerably worldwide. A rapid expansion in production is being observed not only in the United States but also in many other developed and developing countries around the world. Increasing the share of biodiesel in transportation fuels may decrease the net emission of CO_2 and alleviate the global warming problem. Biodiesel fuel is a renewable substitute fuel for petroleum diesel or petrodiesel fuel made from vegetable or animal fats; it can be used in any mixture with petrodiesel fuel, as it has very similar characteristics, but it has lower exhaust emissions. Biodiesel fuel has better properties than petrodiesel fuel; it is renewable, biodegradable, non-toxic, and essentially free of sulfur and aromatics. Biodiesel seems to be a realistic fuel for the future, and has become more attractive recently because of its environmental benefits. Biodiesel is an environmentally friendly fuel that can be used in any diesel engine without modification.

Typical raw materials of biodiesel are rapeseed oil, soybean oil, sunflower oil and palm oil. Beef and sheep tallow and poultry oil from animal sources and cooking oil are also sources of raw materials. There are various other biodiesel sources: almond, andiroba (*Carapa guianensis*), babassu (*Orbignia* sp.), barley, camelina (*Camelina sativa*), coconut, copra, cumaru (*Dipteryx odorata*), *Cynara cardunculus*, fish oil, groundnut, *Jatropha curcas*, karanja (*Pongamia glabra*), laurel, *Lesquerella fendleri*, *Madhuca indica*, microalgae (*Chlorella vulgaris*), oat, piqui (*Caryocar* sp.), poppy seed, rice, rubber seed, sesame, sorghum, tobacco seed, and wheat (Pinto et al., 2005).

The biggest advantage of biodiesel is the environmentally friendliness that it has over gasoline and petroleum diesel. The advantages of biodiesel as a diesel fuel are its portability, ready availability, renewability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number, and higher biodegradability (Ma and Hanna, 1999). The main advantages of biodiesel given in the literature include its domestic origin, its potential for reducing a given economy's dependency on imported petroleum, biodegradability, high flash point, and inherent lubricity in the neat form.

Biodiesel can be made from domestically produced, renewable oilseed crops such as soybean, rapeseed, and sunflower. The risks of handling, transporting, and storing biodiesel are much lower than those associated with petrodiesel. Biodiesel is the only alternative fuel in which low-concentration biodiesel–diesel blends run on conventional unmodified engines. It can be stored anywhere that petroleum diesel fuel is stored. Biodiesel is safe to handle and transport because it is as biodegradable as sugar and has a high flash point compared to petroleum diesel fuel. Biodiesel can be used alone or mixed in any ratio with petroleum diesel fuel. The most common blend is a mix of 20% biodiesel with 80% petroleum diesel, or B20 in recent scientific investigations; however, in Europe the current regulation foresees a maximum 5.75% of biodiesel.

The commercial biodiesel fuel significantly reduced PM exhaust emissions (75–83%) compared to the petrodiesel base fuel. However, NO_x exhaust emissions increased slightly with commercial biodiesel compared to the base fuel. The chain length of the compounds had little effect on NO_x and PM exhaust emissions, while the influence was greater on HC and CO, the latter being reduced with decreasing chain length. Non-saturation in the fatty compounds causes an increase in NO_x exhaust emissions.

Many studies on the performances and emissions of compression ignition engines, fueled with pure biodiesel and blends with diesel fuel, have been conducted and are reported in the literature (Laforgia and Ardito, 1994). Fuel characterization data show some similarities and differences between biodiesel and petrodiesel fuels. The sulfur content of petrodiesel is 20 to 50 times that of biodiesel. Biodiesel has demonstrated a number of promising characteristics, including reduction of exhaust emissions.

For soybean-based biodiesel at this concentration, the estimated emission impacts for percent change in emissions of NO_x, particular matter (PM), HC, and CO were +20%, –10.1%, –21.1%, and –11.0%, respectively (EPA, 2002). The use of blends of biodiesel and diesel oil are preferred in engines in order to avoid some problems related to the decrease of power and torque, and to the increase of NO_x emissions (a contributing factor in the localized formation of smog and ozone) that occurs with an increase in the content of pure biodiesel in a blend. Emissions of all pollutants except NO_x appear to decrease when biodiesel is used. The use of biodiesel in a conventional diesel engine dramatically reduces the emissions of unburned hydrocarbons, carbon dioxide, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons, ozone-forming hydrocarbons, and particulate matter. The net contribution of carbon dioxide from biomass combustion is small.

Biodegradability of biodiesel has been proposed as a solution for the waste problem. Biodegradable fuels such as biodiesels have an expanding range of potential applications and they are environmentally friendly. Therefore, there is growing interest in degradable diesel fuels that degrade more rapidly than conventional disposable fuels. Biodiesel is non-toxic and degrades about four times faster than petrodiesel. Its oxygen content improves the biodegradation process, leading to a decreased level of quick biodegradation. About 90 to 98% of biodiesel is mineralized in 21 to 28 days under aerobic as well as anaerobic conditions. The biodegradabilities of several biodiesels in the aquatic environment show that all biodiesel fuels are readily biodegradable. In one study, after 28 days all biodiesel fuels were 77 to 89% biodegraded; diesel fuel was only 18% biodegraded. The enzymes responsible for the dehydrogenation/oxidation reactions that occur in the process of degradation recognize oxygen atoms and attack them immediately.

Biodiesel methyl esters improve the lubrication properties of the diesel fuel blend. Fuel injectors and some types of fuel pumps rely on fuel for lubrication. Biodiesel reduced long-term engine wear in test diesel engines to less than half of what was observed in engines running on current low-sulfur diesel fuel. Lubricity properties of fuel are important for reducing friction wear in engine components normally lubricated by the fuel rather than crankcase oil (Ma and Hanna, 1999; Demirbas, 2003). Biodiesel provides significant lubricity improvement over petroleum diesel fuel. Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel. Even biodiesel levels below 1% can provide up to a 30% increase in lubricity. Lubricity results of biodiesel and petroleum diesel using industry test methods indicate that there is a marked improvement in lubricity when biodiesel is added to conventional diesel fuel.

Biodiesels are mono-alkyl esters containing approximately 10% oxygen by weight. The oxygen improves the efficiency of combustion, but it takes up space in the blend and therefore slightly increases the apparent fuel consumption rate observed while operating an engine with biodiesel. The high combustion temperature at high engine speed becomes the dominant factor, making both heated and unheated fuel to acquire the same temperature before fuel injection. Brake thermal efficiency is better in the dual fuel operation and with the methyl ester of vegetable oil as compared to the blend. In an earlier study (Canakci et al., 2006), the tests were performed with commercial diesel fuel and biodiesel. The maximum brake power values of biodiesel and diesel were 4.390 and 5.208 kW obtained at 2750 and 2500 rpm, respectively. According to these values, the commercial diesel fuel has the greatest brake power.

The major disadvantages of biodiesel are its higher viscosity, lower energy content, higher cloud point and pour point, higher nitrogen oxide (NO_x) emissions, lower engine speed and power, injector coking, engine compatibility, and high price (Demirbas, 2008c). The biodiesels on the average decrease power by 5% compared to that of diesel at the rated load. The maximum torque values are about 21.0 Nm at 1500 rpm for the diesel fuel, and 19.7 Nm at 1500 rpm for the biodiesel. The torque values of commercial diesel fuel are greater than those of biodiesel. Peak torque applies less to biodiesel fuels than it does to No. 2 diesel fuel but occurs at lower engine speed and generally its torque curves are flatter.

The specific fuel consumption values of biodiesel are greater than those of commercial diesel fuel. The effective efficiency and effective pressure values of commercial diesel fuel are greater than those of biodiesel (Canakci et al., 2006). Important operating disadvantages of biodiesel in comparison with petrodiesel are cold-start problems, the lower energy content, higher copper strip corrosion and fuel pumping difficulty from higher viscosity. Fuel consumption at full load condition and low speeds generally is high. Fuel consumption first decreases and then increases with increasing speed. The reason is that, the produced power in low speeds is low and the main part of fuel is consumed to overcome the engine friction.

The effects of oxidative degradation caused by contact with ambient air (autoxidation) during long-term storage present a legitimate concern in terms of maintaining the fuel quality of biodiesel. Transunsaturated fatty acids, or *transfats*, are solid fats produced artificially by heating liquid vegetable oils in the presence of metal catalysts and hydrogen. This process, partial hydrogenation, causes carbon atoms to bond in a straight configuration and remain in a solid state at room temperature. Physical properties that are sensitive to the effects of fatty oil oxidation include viscosity, refractive index, and dielectric constant. In oxidative instability, the methylene group ($-CH_2-$) carbons between the olefinic carbons are the sites of first attack.

Oxidation to CO_2 of biodiesel results in the formation of hydroperoxides. The formation of a hydroperoxide follows a well-known peroxidation chain mechanism. Oxidative lipid modifications occur through lipid peroxidation mechanisms in which free radicals and reactive oxygen species abstract a methylene hydrogen atom from polyunsaturated fatty acids, producing a carbon-centered lipid radical. Spontaneous rearrangement of the 1,4-pentadiene yields a conjugated diene, which reacts with molecular oxygen to form a lipid peroxyl radical.

3.6 Biogas

Biogas is an environment friendly, clean, cheap and versatile gaseous fuel. It is mainly a mixture of methane and carbon dioxide obtained by anaerobic digestion of biomass, sewage sludge, animal wastes, and industrial effluents. Anaerobic digestion occurs in the absence of air and is typically carried out for a few weeks. Typical compositions of biogas and landfill gas are given in Table 3.7. CH_4 and CO_2 make up around 90% of the gas volume produced, both of which are greenhouse gases. However, CO_2 is recycled back by the plants, but methane can contribute to global warming. Hence, the capture and fuel use of biogas is beneficial in two ways: (a) fuel value, and (b) conversion of CH_4 into CO_2, a plant-recyclable carbon.

Anaerobic digestion (AD) is the conversion of organic material directly to a gas, termed biogas, a mixture of mainly methane and carbon dioxide with small quantities of other gases such as hydrogen sulfide. Methane is the major component of the biogas used in many homes for cooking and heating. The biogas has a chemical composition close to that of natural gas. A biodigester, or a biogas plant,

Table 3.7 Composition of biogas and landfill gas

Component	Chemical formula	Landfill gas	Biogas
Methane (% by vol.)	CH_4	40–60	55–70
Carbon dioxide (% by vol.)	CO_2	20–40	30–45
Nitrogen (% by vol.)	N_2	2–20	0–2
Oxygen (% by vol.)	O_2	< 1	< 1
Heavier hydrocarbons (% by vol.)	C_nH_{2n+2}	< 1	0
Hydrogen sulfide (ppm)	H_2S	20–200	100–500
Ammonia (NH_3) (ppm)	NH_3	0	80–100
Volatile organic compounds (% by vol.)	–	0.25–0.50	0

is a physical structure used to provide an anaerobic condition which stimulates various chemical and microbiological reactions resulting in the decomposition of input slurries and the production of biogas—mainly methane (Demirbas and Ozturk, 2004).

Biogas can be used after appropriate gas cleanup as a fuel for engines, gas turbines, fuel cells, boilers, industrial heaters, other processes, or for the manufacturing of chemicals. Before landfilling, treatment or stabilization of biodegradable materials can be accomplished by a combination of anaerobic digestion followed by aerobic composting.

The same types of anaerobic bacteria that produced natural gas also produce methane today. Anaerobic bacteria are some of the oldest forms of life on earth. They evolved before the photosynthesis of green plants released large quantities of oxygen into the atmosphere. Anaerobic bacteria break down or digest organic material in the absence of oxygen and produce biogas as a waste product.

The first methane digester plant was built at a leper colony in Bombay, India, in 1859 (Meynell, 1976). Most of the biogas plants utilize animal dung or sewage. A schematic of a biogas plant utilizing cow dung is illustrated in Fig. 3.5 (Balat, 2008). Anaerobic digestion is a commercially proven technology and is widely used for treating high moisture content organic wastes including +80–90% moisture. Biogas can be used directly in spark ignition gas engines (SIGEs) and gas turbines. Used as a fuel in SIGE to produce electricity only, the overall conversion efficiency from biomass to electricity is about 10–16% (Demirbas, 2006).

Aerobic conversion includes most commercial composting and activated sludge wastewater treatment processes. Aerobic conversion uses air or oxygen to support the metabolism of the aerobic microorganisms degrading the substrate. Nutritional considerations are also important to the proper functioning of aerobic processes. Aerobic processes operate at much higher reaction rates than anaerobic processes and produce more cell mass, but generally do not produce useful fuel gases. Aerobic decomposition can occur from as low as near freezing to about 344 K.

Respiration refers to those biochemical processes in which organisms oxidize organic matter and extract the stored chemical energy needed for growth and repro-

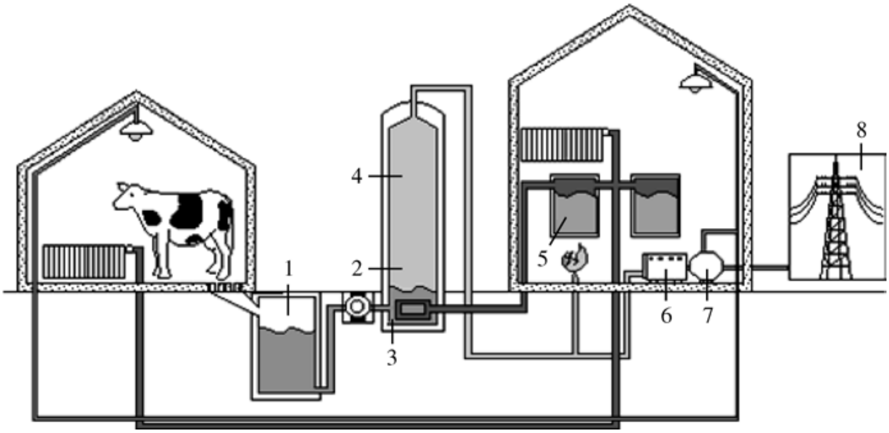

Fig. 3.5 Schematic of biogas plant utilizing cow dung: *1* Compost storage, *2* pump, *3* internal heater, *4* digester, *5* combustor, *6–8* power generator

duction. Respiration patterns may be subdivided into two major groups, based on the nature of the ultimate election acceptor. Although alternative pathways exist for the oxidation of various organic substrates, it is convenient to consider only the degradation of glucose. The breakdown of glucose is via the Embden–Meyerhof–Parnas glycolytic pathway, which yields 2 moles each of pyruvate, ATP, and reduced nicotinamide adenine dinucleotide (NAD) per mole of glucose.

Under aerobic conditions, the pyruvate is oxidized to CO_2 and H_2O via the tricarboxylic acid or Krebs cycle and the electron transport system. The net yield for glycolysis followed by complete oxidation is 38 moles ATP per mole glucose, although there is evidence that the yield for bacteria is 16 moles ATP per mole glucose (Aiba et al., 1973). Thus, 673 kcal are liberated per mole glucose, much of which is stored as ATP.

For anaerobic systems, methane gas is an important product. Depending on the type and nature of the biological components, different yields can be obtained for different biodegradable wastes. For pure cellulose, for example, the biogas product is 50% methane and 50% carbon dioxide. Mixed waste feedstocks yield biogas with methane concentrations of 40–60% (by volume). Fats and oils can yield biogas with 70% methane content.

Anaerobic digestion functions over a wide temperature range from the so-called psychrophilic temperature near 283 K to extreme thermophilic temperatures above 344 K. The temperature of the reaction has a very strong influence on the anaerobic activity, but there are two optimal temperature ranges in which microbial activity and biogas production rate are highest, the so-called mesophilic and thermophilic ranges. The mesophilic regime is associated with temperatures of about 308 K, the thermophilic regime of about 328 K. Operation at thermophilic temperature allows for shorter retention time and a higher biogas production rate; however, maintaining the high temperature generally requires an outside heat source because anaero-

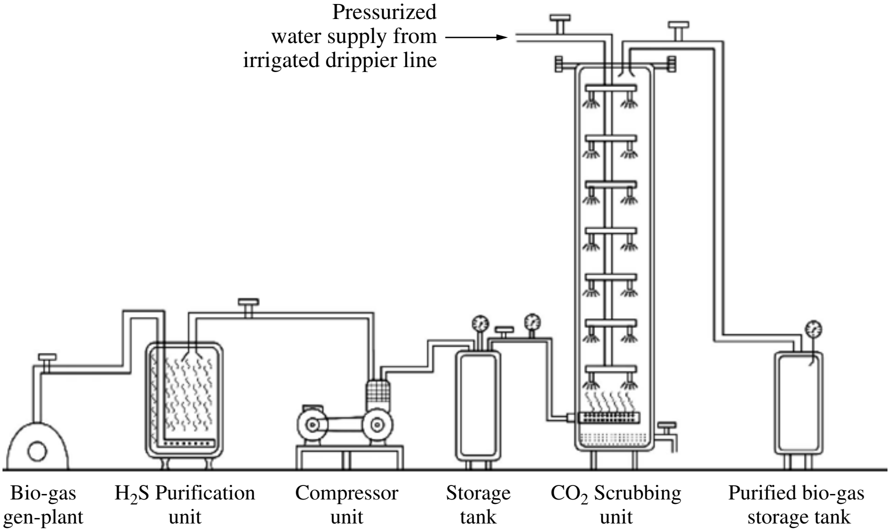

Fig. 3.6 Biogas purification plant

bic bacteria do not generate sufficient heat. Aerobic composting can achieve relatively high temperatures (up to 344 K) without heat addition because reaction rates for aerobic systems are much higher than those for anaerobic systems. If heat is not conducted away from the hot center of a compost pile, then thermochemical reactions can initiate which can lead to spontaneous combustion if sufficient oxygen reaches the hot areas. Managed compost operations use aeration to provide oxygen to the bacteria but also to transport heat out of the pile. The anaerobic digestion of lignocellulosic waste occurs in a three-step process often termed hydrolysis, acetogenesis, and methanogenesis. The molecular structure of the biodegradable portion of the waste that contains proteins and carbohydrates is first broken down through hydrolysis. The lipids are converted to volatile fatty acids and amino acids. Carbohydrates and proteins are hydrolyzed to sugars and amino acids. In acetogenesis, acid-forming bacteria use these byproducts to generate intermediary products such as propionate and butyrate. Further microbial action results in the degradation of these intermediary products into hydrogen and acetate. Methanogenic bacteria consume the hydrogen and acetate to produce methane and carbon dioxide. Figure 3.6 shows a biogas purification plant.

Under anaerobic conditions, various pathways exist for pyruvate metabolism which serve to re-oxidize the reduced hydrogen carriers formed during glycolysis. The ultimate acceptor builds up as a waste product in the culture medium. The end-products of the pathways are: (1) CO_2, ATP, and acetate; (2) CO_2 and ethanol; (3) H_2 and CO_2; (4) CO_2 and 2,3-butylene glycol; (5) CO_2, H_2, acetone, ATP, and butanol; (6) succinate; and (7) lactate. The pathway that occurs depends on the microorganism cultivated and the culture.

3.7 Landfill Gas

Main biorenewable gaseous fuels are biogas, landfill gas, gaseous fuels from pyrolysis and gasification of biomass, gaseous fuels from Fischer–Tropsch synthesis and biohydrogen. There are a number of processes for converting of biomass into gaseous fuels such as methane or hydrogen. One pathway uses plant and animal wastes in a fermentation process leading to biogas from which the desired fuels can be isolated. This technology is established and in widespread use for waste treatment. Anaerobic digestion of biowastes occurs in the absence of air, the resulting gas called a biogas is a mixture consisting mainly of methane and carbon dioxide. Biogas is a valuable fuel which is produced in digesters filled with the feedstock like dung or sewage. The digestion is allowed to continue for a period of ten days to a few weeks. A second pathway uses algae and bacteria that have been genetically modified to produce hydrogen directly instead of the conventional biological energy carriers. Finally, high-temperature gasification supplies a crude gas, which may be transformed into hydrogen by a second reaction step. This pathway may offer the highest overall efficiency.

Contents of domestic solid waste are given in Table 3.8.

Landfill leachate treatment has received significant attention in recent years, especially in municipal areas (Uygur and Kargi, 2004). The generation of municipal solid wastes (MSW) has increased in parallel to rapid industrialization. Approximately 16% of all discarded MSW is incinerated (EPA, 1994); the remainder is disposed of in landfills. Effective management of these wastes has become a major social and environmental concern (Erses and Onay, 2003). Disposal of MSW in sanitary landfills is usually associated with soil, surface water and groundwater contamination when the landfill is not properly constructed. The flow rate and composition of leachate vary from site to site, seasonally at each site and depending on the age of the landfill. Young leachate normally contains high amounts of volatile fatty acids (Timur and Ozturk, 1999). MSW statistics and management practices including waste recovery and recycling initiatives have been evaluated (Metin et al., 2003). The organic MSW was chemically and biologically characterized, in order to study its behavior during anaerobic digestion, and its pH, biogas production, alkalinity, and volatile fatty acid production was determined by Plaza et al. (1996). Anaerobic digestion of the organic food fraction of MSW, on its own or co-digested with primary sewage sludge, produces high-quality biogas, suitable as renewable energy (Kiely et al., 1997). The processing of MSW (i.e., landfill, incineration, aerobic composting) secures many advantages and limitations (Braber, 1995). The greenhouse gas emissions produced by the uncontrolled releasing of methane from improperly disposed organic waste in a large landfill can be reduced (Al-Dabbas, 1998).

The decomposition in landfills occurs in a series of stages, each of which is characterized by the increase or decrease of specific bacterial populations and the formation and utilization of certain metabolic products. The first stage of decomposition, which usually lasts less than a week, is characterized by the removal of

Table 3.8 Contents of domestic solid waste (wt.% of total)

Component	Lower limit	Upper limit
Paper waste	33.2	50.7
Food waste	18.3	21.2
Plastic matter	7.8	11.2
Metal	7.3	10.5
Glass	8.6	10.2
Textile	2.0	2.8
Wood	1.8	2.9
Leather and rubber	0.6	1.0
Miscellaneous	1.2	1.8

oxygen from the waste by aerobic bacteria (Augenstein and Pacey, 1991). In the second stage, which has been termed the anaerobic acid stage, a diverse population of hydrolytic and fermentative bacteria hydrolyzes polymers, such as cellulose, hemicellulose, proteins, and lipids, into soluble sugars, amino acids, long-chain carboxylic acids, and glycerol (Micales and Skog, 1997).

3.8 Fischer–Tropsch Liquids from Biorenewable Feedstocks

Fischer–Tropsch synthesis (FTS) is a process for producing mainly straight-chain hydrocarbons from a synthesis gas rich in CO and H_2. Catalysts are usually employed. Typical operating conditions for FT synthesis are temperatures of 475–625 K and very high pressure depending on the desired products. The product range includes light hydrocarbons such as methane (CH_4) and ethane (C_2H_6), propane (C_3H_8) butane (C_4H_{10}), gasoline (C_5–C_{12}), diesel (C_{13}–C_{22}), and light and waxes (C_{23}–C_{33}). The distribution of the products depends on the catalyst and the process conditions (temperature, pressure, and residence time). The synthesis gas must have very low tar and particulate matter content. Biomass-derived synthesis gas for FT liquid production is feasible and is not limited due to gas cleaning issues. FT from natural gas and ethanol from biomass may become widespread. The FT liquids will penetrate if there are large amounts of stranded natural gas selling for very low prices at the same time that petroleum is expensive or extremely low sulfur is required in diesel fuel (Demirbas, 2005).

The FTS was established in 1923 by German scientists Franz Fischer and Hans Tropsch. The main aim of FTS is the synthesis of long-chain hydrocarbons from CO and H_2 gas mixture. The FTS is described by the set of equations (Schulz, 1999):

$$nCO + (n + m/2)\, H_2 \rightarrow C_nH_m + nH_2O \qquad (3.2)$$

where n is the average length of the hydrocarbon chain and m is the number of hydrogen atoms per carbon. All reactions are exothermic and the product is a mixture of different hydrocarbons in that paraffin and olefins are the main parts.

Fischer–Tropsch (FT) liquid fuel can be used as an alternate to diesel fuel. The FT catalytic conversion process can be used to synthesize diesel fuels from a variety of feedstocks, including coal, natural gas and biomass. The alternate fuel source is coal, indirectly converted to diesel fuel. The FT process uses various catalysts to produce linear hydrocarbons and oxygenates, including unrefined gasoline, diesel, and wax ranges. Gasification followed by FTS is currently the most promising method for upgrading low-value coal and biomass to high-value liquid fuels and chemicals. The total biomass produced each year as waste material from agriculture and forest operations could be converted into roughly 40 billion gallon per year liquid fuels, roughly 25% of the current US gasoline usage).

Synthetic FT diesel fuels can have excellent autoignition characteristics. The FT diesel is composed of only straight-chain hydrocarbons and has no aromatics or sulfur. Reaction parameters are temperature, pressure and H_2/CO ratio. FT product composition is strongly influenced by catalyst composition: the yield of paraffins is higher with cobalt catalytic run and the yield of olefins and oxygenates is higher with ironcatalytic run.

Basic FT reactions are:

$$nCO + 2nH_2 \rightarrow n(\text{-}CH_2\text{-}) + nH_2O \qquad (3.3)$$

$$nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \qquad (3.4)$$

Catalysts and reactors have been extensively investigated for liquid phase Fischer–Tropsch synthesis (Davis, 2002). The synthetic Fischer–Tropsch diesel fuel can provide benefits in terms of both PM and NO_x emissions (May, 2003). Properties of FT and No. 2 diesel fuels are given in Table 3.9.

FT is most compatible with existing distribution for conventional diesel and only minimal adjustments are required to obtain optimal performance from existing diesel engines. Physical properties of FT are very similar to No. 2 diesel fuel, and its chemical properties are superior in that the FT process yields middle distillates that, if correctly processed (as through a cobalt-based catalyst), contain no aromatics or sulfur compounds.

Table 3.9 Properties of Fischer–Tropsch (FT) diesel and No. 2 diesel fuels

Property	Fischer–Tropsch diesel	No. 2 petroleum diesel
Density, g/cm³	0.7836	0.8320
Higher heating value, MJ/kg	47.1	46.2
Aromatics, %	0–0.1	8–16
Cetane number	76–80	40–44
Sulfur content, ppm	0–0.1	25–125

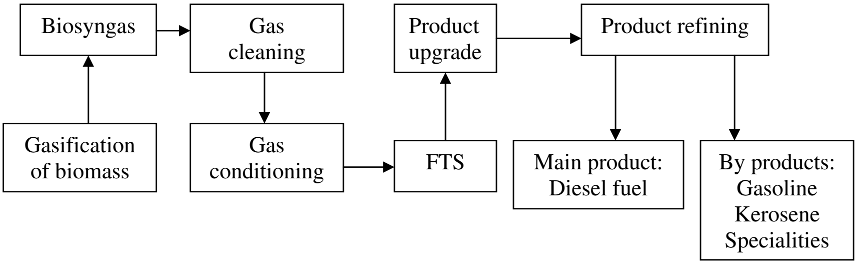

Fig. 3.7 Production of diesel fuel from biosyngas by Fischer–Tropsch synthesis (FTS)

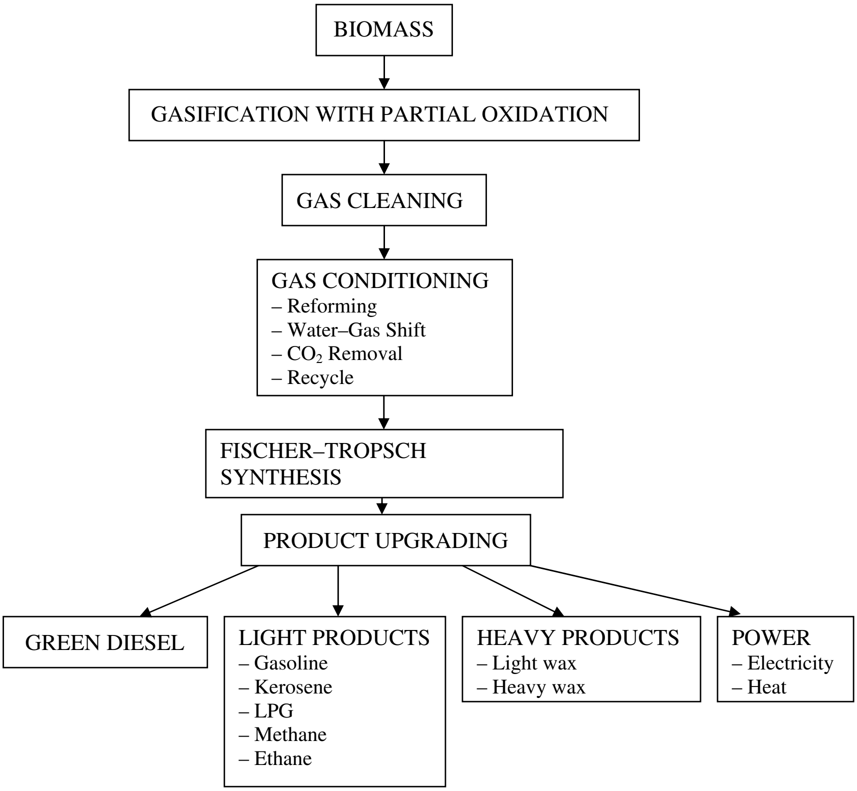

Fig. 3.8 Green diesel and other products from biomass via Fischer–Tropsch synthesis

Figure 3.7 shows the production of diesel fuel from biosyngas by FTS. The design of a biomass gasifier integrated with a FTS reactor must be aimed at achieving a high yield of liquid hydrocarbons. For the gasifier, it is important to avoid methane formation as much as possible, and convert all carbon in the biomass to mainly carbon monoxide and carbon dioxide (Prins et al., 2004).

To produce biosyngas from a biomass fuel the following procedures are necessary: (a) gasification of the fuel, (b) cleaning of the product gas, and (c) usage of the synthesis gas to produce chemicals, (d) usage of the synthesis gas as energy carrier in fuel cells. Figure 3.8 shows the green diesel and other products from biomass via Fischer–Tropsch synthesis.

Supercritical fluids (SCFs) offer several advantages as reaction media for catalytic reactions. These advantages include the ability to manipulate the reaction environment through simple changes in pressure to enhance solubility of reactants and products, to eliminate interphase transport limitations, and to integrate reaction and separation unit operations. Benefits derived from the SCF phase Fischer–Tropsch synthesis (SCF–FTS) involve the gas-like diffusivities and liquid-like solubilities, which together combine the desirable features of the gas- and liquid-phase FT synthesis routes.

Steady-state operation was quickly achieved under SCF conditions and the SCF–FT process has a marked effect on the hydrocarbon product distribution with a shift to higher carbon number products owing to enhanced heat and mass transfer from the catalyst surface. In addition, an obvious difference in the olefin content was observed where the 1-olefin content in the SCF phase was always higher than in the gas phase. Based on the experimental observations, a mechanistic explanation is provided for the difference of the reaction behavior under supercritical and gas-phase environments.

Summary

The term biofuel refers to liquid, gas and solid fuels predominantly produced from biomass. Biofuels affect a wide range of topics, including energy security, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Biofuels include bioethanol, biomethanol, vegetable oils, biodiesel, biogas, biosynthetic gas (biosyngas), bio-oil, biochar, Fischer–Tropsch liquids, and biohydrogen. Biofuels offer a number of technical and environmental benefits over conventional fossil fuels, which make them attractive as alternatives for the transport sector. The benefits include greenhouse gas reductions including reduced carbon dioxide emissions, which will contribute to domestic and international targets, the diversification of the fuel sector, biodegradability, sustainability, and an additional market for agricultural products.

Nowadays ethanol is the most popular fuel. The use of ethanol as a motor fuel has as long a history as the car itself. Ethanol can be produced from cellulose feedstocks such as corn stalks, rice straw, sugar cane bagasse, pulpwood, switchgrass; ethanol produced from municipal solid waste is called bioethanol. Methanol is known as wood alcohol. Generally, methanol is easier to find than ethanol. Sustainable methods of methanol production are currently not economically viable. Methanol is produced from synthetic gas or biogas and evaluated as a fuel for internal combustion engines.

Biorefinery is the co-production of a spectrum of bio-based products and energy from biomass. The biorefinery concept is analogous to today's crude oil refinery. Biorefinery is a relatively new term referring to the conversion of biomass feedstock into a host of valuable chemicals and energy with minimal waste and emissions.

Biodiesel is attracting increasing attention worldwide as blending components or direct replacements for diesel fuel in vehicle engines. Biodiesel typically comprises lower alkyl fatty acid (chain length C_{14}–C_{22}), esters of short-chain alcohols, primarily, methanol or ethanol.

Main biorenewable gaseous fuels are biogas, landfill gas, gaseous fuels from pyrolysis and gasification of biomass, gaseous fuels from Fischer–Tropsch synthesis and biohydrogen. There are a number of processes for converting biomass into gaseous fuels such as methane or hydrogen. One pathway uses plant and animal wastes in a fermentation process leading to biogas from which the desired fuels can be isolated.

Biogas is considered a clean, cheap and versatile gaseous fuel that is also environmentally friendly. It is mainly a mixture of methane and carbon dioxide obtained by anaerobic digestion of biomass, sewage sludge, animal wastes, and industrial effluents. Anaerobic digestion occurs in the absence of air and is typically carried out for a few weeks.

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